

APPENDIX C

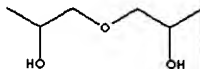
(Serial No. 09/788,164)



DIPROPYLENE GLYCOL

PRODUCT IDENTIFICATION

CAS NO 25265-71-8
 EINECS NO. 246-770-3
 FORMULA $\text{HOC}_3\text{H}_6\text{OC}_3\text{H}_6\text{OH}$
 MOL WT. 134.18
 H.S. CODE



TOXICITY Oral rat LD50: 13000 mg/kg
 SYNONYMS Oxybispropanol; Di-sec-alcohol; Bis(2-hydroxy-propyl)ether;
 DERIVATION byproduct of propylene glycol
 CLASSIFICATION SOLVENT / DIOLS /
 PHYSICAL AND CHEMICAL PROPERTIES
 PHYSICAL STATE clear liquid
 MELTING POINT 78 C
 BOILING POINT 231 C
 SPECIFIC GRAVITY 1.023
 SOLUBILITY IN WATER miscible
 pH
 VAPOR DENSITY 4.63
 AUTOIGNITION
 NFPA RATINGS Health: 0 Flammability: 1 Reactivity: 0
 REFRACTIVE INDEX 1.438 - 1.442
 FLASH POINT 124 C
 STABILITY Stable under ordinary conditions

GENERAL DESCRIPTION & APPLICATIONS

Dipropylene Glycol is a colourless, viscous, practically non-toxic and slightly hygroscopic liquid; melting point -78 C, boiling point 231 C, specific gravity 1.023. It is a isomer mixture of 1,1'-Oxybis(2-propanol) (cas no. 108-61-2), 2-(2-Hydroxypropoxy)-1-propanol (106-62-7) and 2,2'-Oxybis(1-propanol) (110-98-5). Dipropylene glycol is miscible in water, alcohols, esters and almost organic solvents and various vegetable oils. It is produced during the manufacture of propylene glycol from propylene oxide along with tripropylene glycol and higher glycols. Dipropylene Glycol is used as a solvent, coupling agent and chemical intermediate. Dipropylene glycol is used as a component in the production of unsaturated polyester resins, alkyl resins, polyurethane polyols, textile auxiliaries and Dibenzotriazole plasticisers. It is an ingredient of cutting oils, functional fluids, industrial soaps, agricultural insecticidal formulations, defoamers, cosmetics and fragrances. It is used as an additive for carburettor fuels as a lubricant and anti-freezing agent. Dipropylene glycol is used as a solvent for printing inks, cellulose acetate, nitrocellulose, lacquers and coatings. In the refinery industry, it is used as an extraction solvent to extract aromatics.

SALES SPECIFICATION

APPEARANCE clear liquid
 ASSAY 99.0% min
 COLOR, APHA 10 max
 CHLORIDE 5ppm max
 ACIDITY 0.01% max
 WATER 0.1% max
 TRANSPORTATION
 PACKING 200kgs in drum
 HAZARD CLASS Not regulated
 UN NO.

GENERAL DESCRIPTION OF PROPYLENE GLYCOL

Glycol: any of a class of organic chemicals characterized by having separate two hydroxyl (-OH) groups, contribute to high water solubility, hygroscopicity and reactivity with many organic compounds, on usually linear and aliphatic carbon chain. The general formula is $\text{C}_n\text{H}_{2n}(\text{OH})_2$ or $(\text{CH}_2)_n(\text{OH})_2$. The wider meaning names include diols, dihydric alcohols, and dihydroxy alcohols. Polyethylene glycols and polypropylene glycols are sometimes called polyglycols which are derived by polymerization of ethylene oxide and propylene oxide respectively. Polyethylene glycols are water-soluble at all molecular weights, but polypropylene glycols become increasingly less water-soluble at high molecular weights. Mono-, di- and tripropylene glycol, the first three members of a homologous series of propylene glycol, are completely water and ethanol soluble; miscible with most organic solvents including acetone, chloroform and some essential oils; soluble in 12 parts of ether. Propylene glycol is an odorless and colorless liquid; boiling point 188 C, freezing point -39 C. Propylene glycol is prepared by hydrolysis of propylene oxide. Large amount of propylene glycol is used in the plastics industry for the manufacture of polyester fibers and alkyl resins. It is used as a main ingredient in automobile antifreeze and engine-cooling liquids and in brake and hydraulic fluids due to its useful properties of low freezing point, involatility and low corrosive activity. It is used in the preparation of body-care surfactants. Propylene glycol is replacing ethylene glycol and ethanol as it is less toxic than ethylene glycol. Propylene glycol is described as a "generally recognized as safe for use in food, cosmetics, and medicines" by FDA. Propylene glycol USP grade is used as a non-toxic antifreeze in breweries and dairies. It is used as a humectant in foods and cosmetics. It is used as a solvent for colouring or flavouring agents as well as in many oral, injectable or topical pharmaceuticals. Its antibacterial property is applied in the preparation of sanitizing lotions.

SUPPLIERS

Korea SKC Co., Ltd
www.skc.co.kr



APPENDIX D

(Serial No. 09/788,164)

United States Patent [19]
Barthorpe

[11] **Patent Number:** 4,995,982
[45] **Date of Patent:** Feb. 26, 1991

[54] **PROCESS FOR RECOVERING AND
PURIFYING A HIGH MOLECULAR
WEIGHT SULFONATE**

[75] **Inventor:** Richard T. Barthorpe, Littleton,
Colo.

[73] **Assignee:** Marathon Oil Company, Findlay,
Ohio

[21] **Appl. No.:** 430,849

[22] **Filed:** Nov. 1, 1989

[51] **Int. Cl.³** B01D 11/04

[52] **U.S. Cl.** 210/634; 528/493;
528/494; 528/496

[58] **Field of Search** 210/634, 729; 528/493,
528/496, 494

[56] **References Cited**

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vol. 6, 1967, pp. 458, 459 and 461.

Primary Examiner—Frank Spear

Assistant Examiner—Krisanne Shideler

Attorney, Agent, or Firm—Jack L. Hummel; Jack E.
Ebel

[57] **ABSTRACT**

A process for separating a relatively high molecular polymeric sulfonate, such as a polyvinyl sulfonate, from undesirable by-products of sulfonation. An aqueous solution having a polymeric sulfonate dissolved therein is contacted with from about 7.5 to about 40 volume percent of a solvent selected from methanol, ethanol, acetone, or dipropylene glycol monomethyl ether to remove undesirable by-products of sulfonation therefrom and to enhance the molecular weight of the polymeric sulfonate.

14 Claims, 2 Drawing Sheets

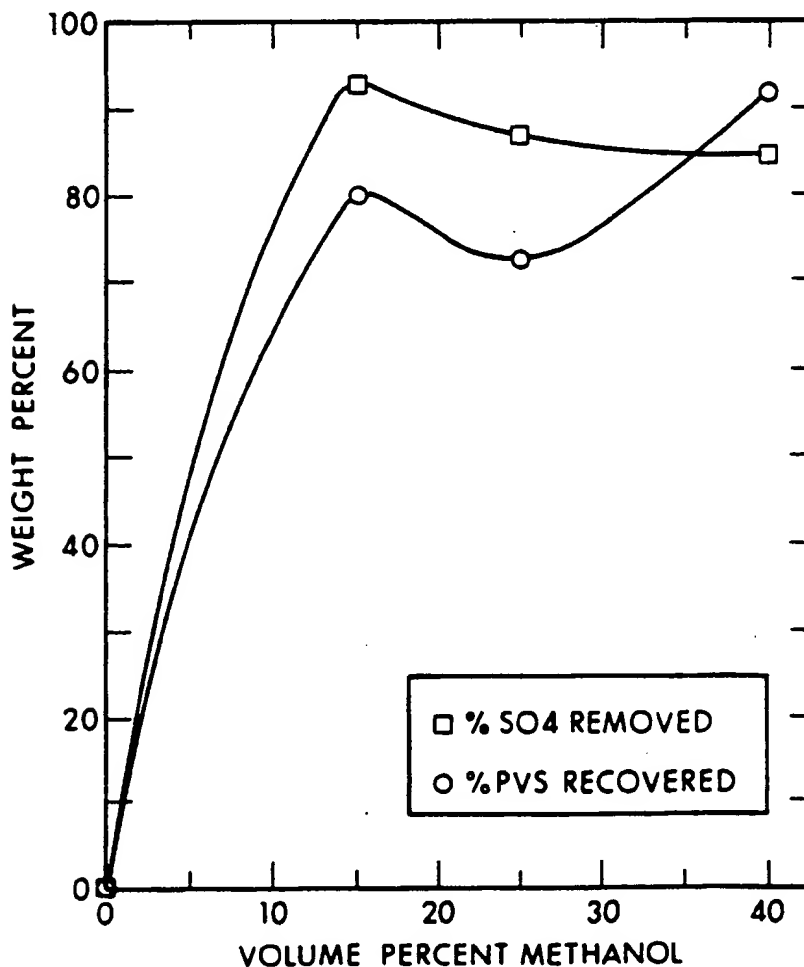
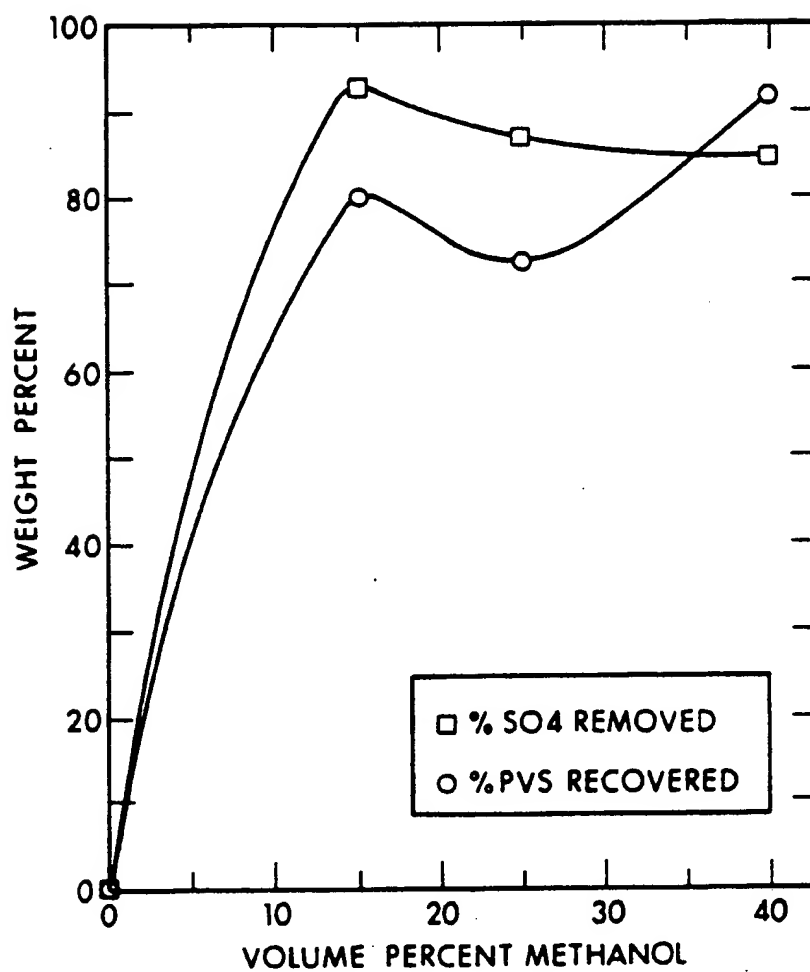
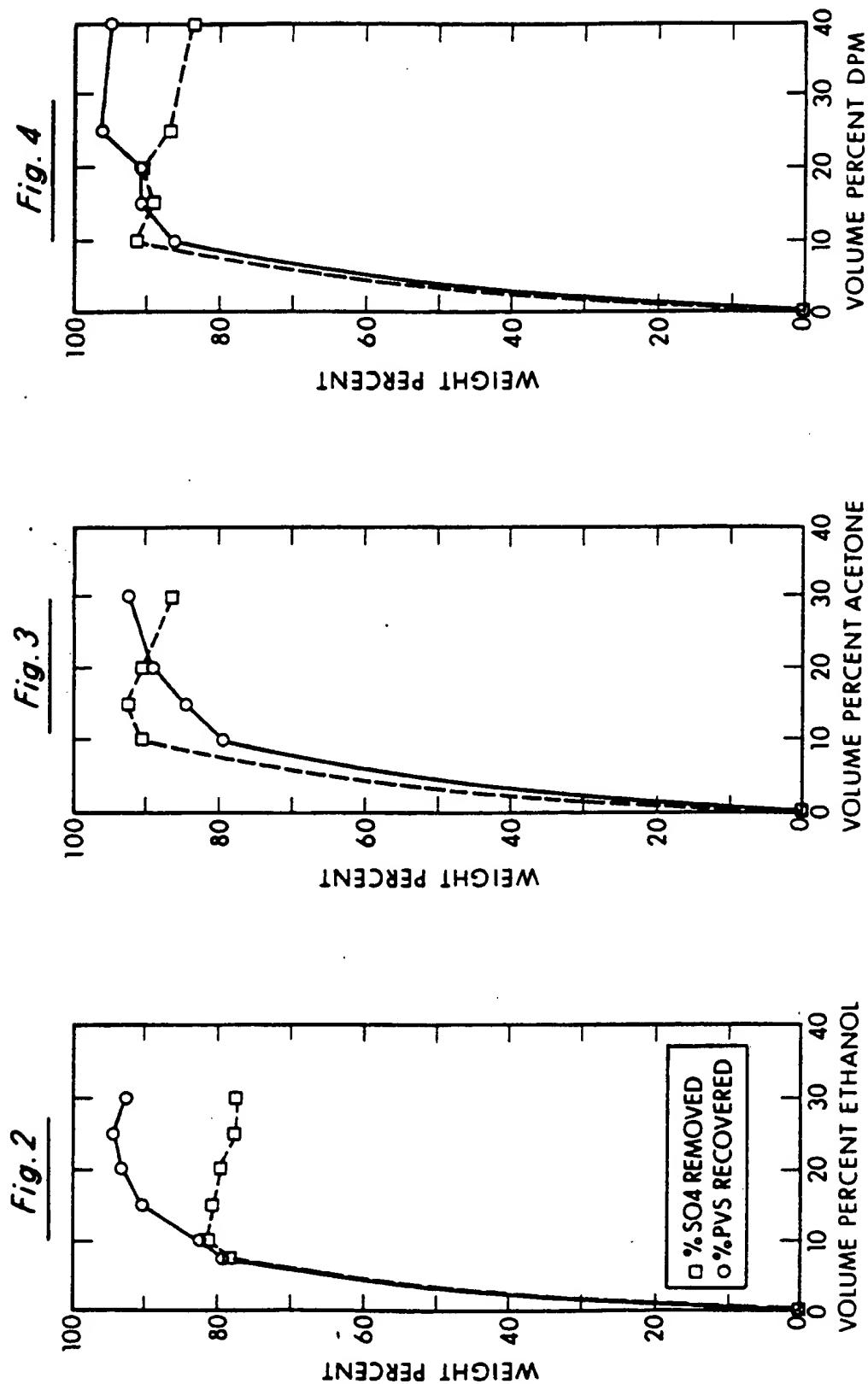


Fig. 1



PROCESS FOR RECOVERING AND PURIFYING A HIGH MOLECULAR WEIGHT SULFONATE

BACKGROUND OF THE INVENTION

The present invention relates to a process for recovering from an aqueous polymerization solution a relatively high molecular weight polymeric sulfonate, such as polyvinyl sulfonate, which is substantially free of undesirable by-products of sulfonation, and more particularly, to such a process wherein the molecular weight of the polymeric sulfonate, such as polyvinyl sulfonate, which is recovered is increased.

Polymeric sulfonates are conventionally polymerized from commercially available solutions containing a monomer in the presence of a suitable catalyst. For example, polyvinyl sulfonate can be polymerized from a commercially available, dilute, e.g. 25-50 weight percent, aqueous solution of vinylsulfonic acid, sodium salt, in the presence of a suitable catalyst, such as ammonium persulfate or sodium bisulfite. The resultant aqueous polymerization solution contains undesirable by-products of sulfonation, such as sulfate ions and hydroxyethyl sulfonate, and unreacted vinylsulfonic acid, sodium salt monomer, in addition to polyvinyl sulfonate. The presence of such undesirable by-products can be extremely deleterious when polyvinyl sulfonate is used as a scale inhibitor. Addition of large quantities of methanol to an aqueous polymerization solution has been advanced to separate polymeric sulfonates, such as polyvinyl sulfonate, therefrom. However, large quantities of methanol will precipitate polymeric sulfonates and unwanted by-products of sulfonation from the solution. Thus, a need exists for a process for separating polymeric sulfonates, such as polyvinyl sulfonate, from an aqueous polymerization solution also containing unwanted by-products of sulfonation.

Accordingly, it is an object of the present invention to provide a process for recovering and purifying a relatively high molecular weight polymeric sulfonate, such as a polyvinyl sulfonate, by selectively separating unwanted by-products of sulfonation, such as sulfate ions and hydroxyethyl sulfonate, from aqueous solutions containing the polymeric sulfonate.

It is a further object of the present invention to provide a process for enhancing the molecular weight of a relatively high molecular weight polymeric sulfonate, such as a polyvinyl sulfonate.

SUMMARY OF THE INVENTION

The present invention provides a process for separating a relatively high molecular weight polymeric sulfonate, such as a polyvinyl sulfonate, from undesirable by-products of sulfonation and for increasing the molecular weight of a relatively high molecular weight polymeric sulfonate, such as a polyvinyl sulfonate. An initial aqueous solution having a polymeric sulfonate, such as a polyvinyl sulfonate, dissolved therein is contacted with from about 7.5 to about 40 volume percent of a solvent selected from methanol, ethanol, acetone, or dipropylene glycol monomethyl ether and forms two distinct phases. The lower phase is separated and water is added thereto to obtain a volume approximately equal to the volume of the initial aqueous solution. Thereafter, the previously selected solvent is added to the separated lower phase in an amount of from about 7.5 to about 40 volume percent of the initial aqueous solution. Two distinct phases are again formed. The resultant lower

phase comprises at least 70 weight percent of the polymeric sulfonate, such as a polyvinyl sulfonate, while at least 70 weight percent of the undesirable by-products of sulfonation are removed therefrom.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the embodiments of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

FIG. 1 is a graph illustrating the weight percent of polyvinyl sulfonate recovered and the weight percent of sulfate ions removed as a function of the volume percent of methanol added to separated lower phases;

FIG. 2 is a graph illustrating the weight percent of polyvinyl sulfonate recovered and the weight percent of sulfate ions removed as a function of the volume percent of ethanol added to separated lower phases;

FIG. 3 is a graph illustrating the weight percent of polyvinyl sulfonate recovered and the weight percent of sulfate ions removed as a function of the volume percent of acetone added to separated lower phases; and

FIG. 4 is a graph illustrating the weight percent of polyvinyl sulfonate recovered and the weight percent of sulfate ions removed as a function of the volume percent of dipropylene glycol monomethyl ether added to separated lower phases.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a process for selectively separating undesirable by-products of sulfonation, such as sulfate ions and hydroxyethyl sulfonate, from an aqueous solution containing a polymeric sulfonate, such as a polyvinyl sulfonate, and to a process which increases the molecular weight of a relatively high molecular weight polymeric sulfonate, such as polyvinyl sulfonate. As utilized throughout this specification, the term 'molecular weight' refers to the weight average molecular weight which is determined from experiments in which each molecule or chain makes a contribution to the measured result. The weight average molecular weights reported in this specification were determined using a size exclusion chromatographic determination of molecular weights which employed a column packed with a polymeric gel. As also utilized throughout this specification, the term "water" refers to preferably fresh water, i.e. water having less than about 1,000 ppm total dissolved solids or to a low salinity brine.

In accordance with the present invention, an aqueous reaction solution having a polymeric sulfonate, for example polyvinyl sulfonate, unreacted monomer, for example sodium vinyl sulfonate monomer, and unwanted by-products of sulfonation dissolved therein is first contacted with a solvent selected from methanol, ethanol, acetone, or dipropylene glycol monomethyl ether by adding the solvent to the aqueous solution. The solvent is added to the aqueous solution in an amount of from about 7.5 volume percent to about 40 volume percent, more preferably from about 10 volume percent to about 25 volume percent, and most preferably from about 15 volume percent to about 25 volume percent. The aqueous solution separates into two distinct phases. An upper phase comprises solvent, a portion of the undesirable by-products of sulfonation, lower molecu-

lar weight components of the polyvinyl sulfonate, and unreacted sodium vinyl sulfonate monomer. A lower phase comprises water, polyvinyl sulfonate, and a portion of undesirable by-products of sulfonation. In accordance with the present invention, the lower phase is separated from the upper phase by any suitable means as will be evident to the skilled artisan. Water is then added to the lower phase in an amount sufficient to increase the volume of the lower phase to the original volume of the aqueous solution. Thereafter, the solvent selected for the initial separation stage is added to the lower phase in a like amount of from about 7.5 volume percent to about 40 volume percent, more preferably from about 10 volume percent to about 25 volume percent, and most preferably from about 15 volume percent to about 25 volume percent to form a distinct upper and lower phase. Once again, the upper phase comprises solvent, a portion of the undesirable by-products of sulfonation, lower molecular weight components of the polyvinyl sulfonate, and unreacted sodium vinyl sulfonate monomer. The lower aqueous phase comprises at least 70 weight percent of the polyvinyl sulfonate while at least about 70 weight percent of the undesirable by-products of sulfonation are removed from the lower phase during the separation process of the present invention. The resultant polyvinyl sulfonate containing aqueous solution can be utilized as a scale inhibitor as described in commonly assigned, co-pending patent application entitled "Polyvinyl Sulfonate Scale Inhibitor" to David O. Falk et al. which was filed concurrently herewith.

While it is preferred to add substantially identical amounts of solvent in the two separation stages of the present invention, the amount of solvent added in the second separation stage can vary by up to about 10 volume percent from the amount of solvent added in the initial separation stage without departing from the scope of the present invention.

The following examples demonstrate the practice and utility of the present invention but are not to be construed as limiting the scope thereof.

EXAMPLE 1

3.75 ml of methanol (15 vol %) are added to 25 ml of an aqueous solution containing 25 wt % of a polyvinyl sulfonate having a molecular weight of about 18,902 in a separating funnel. Two phases are formed and the lower phase is separated from the upper phase through a valve at the bottom of the separating funnel. Enough water is added to the lower phase in a separating funnel to obtain a total volume of 25 ml. 3.75 ml (15 vol %) of methanol is added to the resultant solution. A phase interface is established in approximately 1 minute. After 30 minutes the phases have separated and the lower phase is removed through a valve at the bottom of the separating funnel. A sample of each upper separated phase is analyzed by high pressure liquid chromatography, and it is calculated that the lower phase retains 80 wt % of the polyvinyl sulfonate while 93 wt % of sulfate ions present in the initial solution are removed.

50 ml of an aqueous solution containing 25 wt % of a polyvinyl sulfonate having a molecular weight of about 18,902 is treated by the process of the present invention as set forth above except that 20 ml (40 vol %) of methanol is added to the solution at each of the two separation stages set forth above. This procedure results in 92 wt % of the polyvinyl sulfonate being retained in solution

while 84.3 wt % of the sulfate ions are removed therefrom.

The process of the present invention as set forth above was repeated on an aqueous solution containing 25 wt % of a polyvinyl sulfonate having a molecular weight of about 18,902 except that approximately 25 vol % methanol was added to the aqueous solution containing polyvinyl sulfonate at each separation stage, and the solution was allowed to separate into two phases for approximately 1 hour after each such addition. This procedure results in an aqueous solution of polyvinyl sulfonate in which 72 wt % of the polyvinyl sulfonate is recovered while 87 wt % of the sulfate ions are removed therefrom. The results of such analysis are depicted in FIG. 1.

EXAMPLE 2

Various volume percents of ethanol are each added to separate graduated cylinders containing 10 ml of an aqueous solution containing 25 wt % of a polyvinyl sulfonate having a molecular weight of about 18,902. Each resultant solution is allowed to separate into an upper and lower phase for about 2 hours, and each upper phase is separated with a graduated syringe having a 1/16 inch stainless steel tube. Water is added to each remaining lower phase to obtain 10 ml total volume and varying volume percentages of ethanol which are identical to those previously added are each added to the respective graduated cylinders. Each resultant solution is allowed to separate into two phases for approximately 2 hours and each resultant upper phase is separated with a graduated syringe. Each remaining lower phase is diluted to 10 ml total volume upon the addition of water and is analyzed by high pressure liquid chromatography. The results of such analysis are depicted in FIG. 2.

EXAMPLE 3

Various volume percents of acetone are each added to separate graduated cylinders containing 10 ml of an aqueous solution containing 25 wt % of a polyvinyl sulfonate having a molecular weight of about 18,902. Each resultant solution is allowed to separate into upper and lower phases for about 2 hours, and each upper phase is separated with a graduated syringe having a 1/16 inch stainless steel tube. Water is added to each remaining lower phase to obtain a 10 ml total volume and varying volume percentages of acetone which are identical to those previously added are each added to the separate graduated cylinders. Each resultant solution is allowed to separate into two phases for approximately 2 hours and each upper phase is separated with a graduated syringe. Each remaining lower phase is diluted to 10 ml total volume upon the addition of water and is analyzed by high pressure liquid chromatography. The results of such analysis are depicted in FIG. 3.

EXAMPLE 4

Various volume percents of dipropylene glycol monomethyl ether are each added to separate graduated cylinders containing 10 ml of an aqueous solution containing 25 wt % of a polyvinyl sulfonate having a molecular weight of about 12,191. Each resultant solution is allowed to separate into an upper and lower phase for about 2 hours, and each upper phase is separated with a graduated syringe having a 1/16 inch stainless steel tube. Water is added to each remaining lower phase to obtain a 10 ml total volume and varying volume per-

centages of dipropylene glycol monomethyl ether which are identical to those previously added are each added to the separate graduated cylinders. Each resultant solution is allowed to separate into two phases for approximately 2 hours and each upper phase is separated with a graduated syringe. Each remaining lower phase is diluted to 10 ml total volume upon the addition of water and is analyzed by high pressure liquid chromatography. The results of such analysis are depicted in FIG. 4.

As indicated by the results of Examples 1-4, the two-stage separation process of the present invention results in greater than 70 wt % of the polyvinyl sulfonate being retained in solution while greater than 70 wt % of the undesirable by-products of sulfonation, e.g. sulfate ions, ethanol, acetone, or dipropylene glycol monomethyl ether is added to an aqueous solution having a polyvinyl sulfonate dissolved therein in an amount of from about 10 to about 80 vol % of the total volume of the solution to which the solvent is added. Above about 80 vol %, the cost of solvent and the problem in disposing of the solvent render the use of solvent uneconomical and undesirable. While methanol is the least expensive of the solvents suitable for use in the process of the present invention, methanol is also the most toxic and flammable of the solvents listed. And although dipropylene glycol monomethyl ether is the most expensive, it is non-flammable and is relatively non-toxic.

EXAMPLE 5

The procedure set forth first in Example 1 is repeated utilizing the addition of 25 vol % of methanol. The molecular weight of the polyvinyl sulfonate dissolved in the initial aqueous solution, the polyvinyl sulfonate in each separated upper phase, and the molecular weight of the polyvinyl sulfonate in the resultant aqueous solution are analyzed. The molecular weight of the initial polyvinyl sulfonate is determined to be about 12,191. The molecular weight of the polyvinyl sulfonate in the upper phase resulting from the first stage of the separation process of the present invention is determined to be about 4,855. The molecular weight of the polyvinyl sulfonate in the upper phase of the second stage of the separation process of the present invention is determined to be about 5,189. The molecular weight of the polyvinyl sulfonate in the solution obtained utilizing the process of the present invention is determined to be about 15,049.

As indicated by the results of Example 5, the process of the present invention increases the molecular weight of polyvinyl sulfonate by removing lower molecular weight components of polyvinyl sulfonate during each separation stage. In general, the process of the present invention removes molecular weight components having a molecular weight less than about 5,000. Therefore, the largest increase in molecular weight will be obtained when the process of the present invention is utilized to separate lower molecular weight fractions from polyvinyl sulfonate having a molecular weight greater than 10,000.

Throughout the description, the process of the present invention has been characterized as suitable for recovering, purifying, and enhancing the molecular weight of a polymeric sulfonate, such as a polyvinyl sulfonate. As will be evident to those skilled in the art, the process of the present invention is equally applica-

ble to recover, purify, and enhance the molecular weight of copolymers of polyvinyl sulfonates as well as other polymeric sulfonates, such as polystyrene sulfonate and copolymers thereof and 2-acrylamide, 2-methylpropane sulfonic acid and copolymers thereof.

While the foregoing preferred embodiments of the invention have been described and shown, it is understood that the alternatives and modifications, such as those suggested and others, may be made thereto and fall within the scope of the invention.

I claim:

1. A process for recovering and purifying a polymeric sulfonate containing aqueous solution consisting essentially of:

- (a) adding to an aqueous solution having a polymeric sulfonate and deleterious by-products of sulfonation dissolved therein a sulfonate selected from methanol, ethanol, acetone or dipropylene glycol monomethyl ether, in a first amount of from about 7.5 to about 40 volume percent of said aqueous solution, said aqueous solution to which said solvent has been added in said first amount forming a first upper phase and a first lower aqueous phase;
- (b) separating said first upper phase from said first lower aqueous phase;
- (c) adding water to said first lower aqueous phase in an amount sufficient to obtain a volume of said first lower aqueous phase which is approximately equal to the volume of said aqueous solution;
- (d) adding said solvent to said first lower aqueous phase in a second amount of from about 7.5 to about 40 volume percent of the volume of said aqueous solution thereby forming a second upper phase and a second lower aqueous phase; and
- (e) separating said second lower aqueous phase from said second upper phase, said second lower aqueous phase having a majority of said polymeric sulfonate dissolved therein while said first and said second upper phases having a majority of said deleterious by-products of sulfonation dissolved therein.

2. The process of claim 1 wherein said polymeric sulfonate is a polyvinyl sulfonate.

3. The process of claim 2 wherein at least 70 weight percent of said polyvinyl sulfonate is dissolved in said second lower aqueous phase.

4. The process of claim 1 wherein at least 70 weight percent of said deleterious by-products of sulfonation are dissolved in said first and said second upper phases.

5. The process of claim 1 wherein said first and said second amounts are from about 10 to about 25 volume percent.

6. The process of claim 5 wherein said first and said second amounts are from about 15 to about 25 volume percent.

7. The process of claim 1 wherein said second amount is substantially equal to said first amount.

8. The process of claim 1 wherein said aqueous solution further has unreacted sulfonate monomer dissolved therein and said first and said second upper phases have a portion of said unreacted sulfonate monomer dissolved therein.

9. A process for enhancing the molecular weight of a polymeric sulfonate which is contained in an aqueous solution consisting essentially of:

- (a) adding to an aqueous solution having a polymeric sulfonate dissolved therein a solvent selected from methanol, ethanol, acetone or dipropylene glycol

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- monomethyl ether in a first amount of from about 7.5 to about 40 volume percent of said solution thereby forming a first upper phase and a first lower aqueous phase, said polymeric sulfonate having a first molecular weight;
- (b) separating said first lower aqueous phase from said first upper phase;
- (c) adding water to said first lower aqueous phase in an amount sufficient to obtain a volume of said first lower aqueous phase approximately equal to the volume of said aqueous solution;
- (d) adding said solvent to said first lower aqueous phase in a second amount of from about 7.5 to about 40 volume percent of the volume of said aqueous solution thereby forming a second upper phase and a second lower aqueous phase; and
- (e) separating said second lower aqueous phase from said second upper phase, said second lower aque-

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- ous phase having a majority of said polymeric sulfonate dissolved therein, said majority of said polymeric sulfonate having a second molecular weight which is greater than said first molecular weight.
10. The process of claim 9 wherein said polymeric sulfonate is a polyvinyl sulfonate.
11. The process of claim 10 wherein said polyvinyl sulfonate has a first or second molecular weight greater than 10,000.
12. The process of claim 9 wherein said first and said second amounts are from about 10 to about 25 volume percent.
13. The process of claim 12 wherein said first and said second amounts are from about 15 to about 25 volume percent.
14. The process of claim 9 wherein said second amount is substantially equal to said first amount.
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US005610132A

United States Patent [19][11] **Patent Number:** **5,610,132****Momoda et al.**[45] **Date of Patent:** **Mar. 11, 1997**[54] **CLEANING AGENT FOR REMOVING FATS
AND OILS FROM METAL SURFACES**[75] Inventors: **Kayo Momoda, Tsukuba; Syuji Baba,**
Tokuyama, both of Japan[73] Assignee: **Tokuyama Corporation,**
Yamaguchi-ken, Japan[21] Appl. No.: **493,460**[22] Filed: **Jun. 22, 1995**[30] **Foreign Application Priority Data**

Jun. 24, 1994 [JP] Japan 6-142812

[51] Int. Cl.⁶ **C11D 7/50; C11D 7/26**[52] U.S. Cl. **510/506; 510/245; 510/365;**
134/40[58] **Field of Search** 252/162, 170,
252/173, 174.21, 174.22, DIG. 8, DIG. 10;
510/506, 245, 365; 134/40[56] **References Cited****U.S. PATENT DOCUMENTS**

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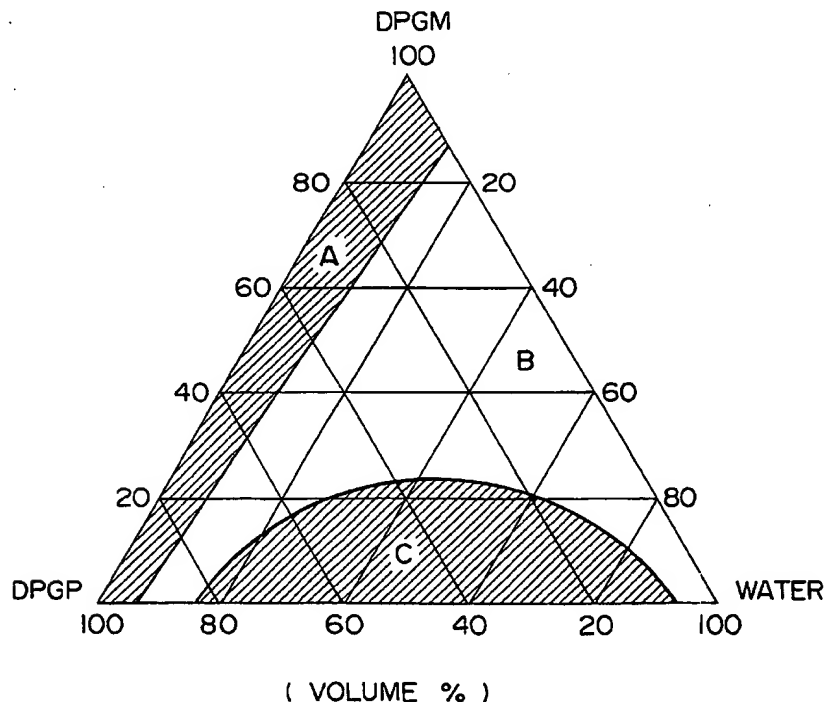
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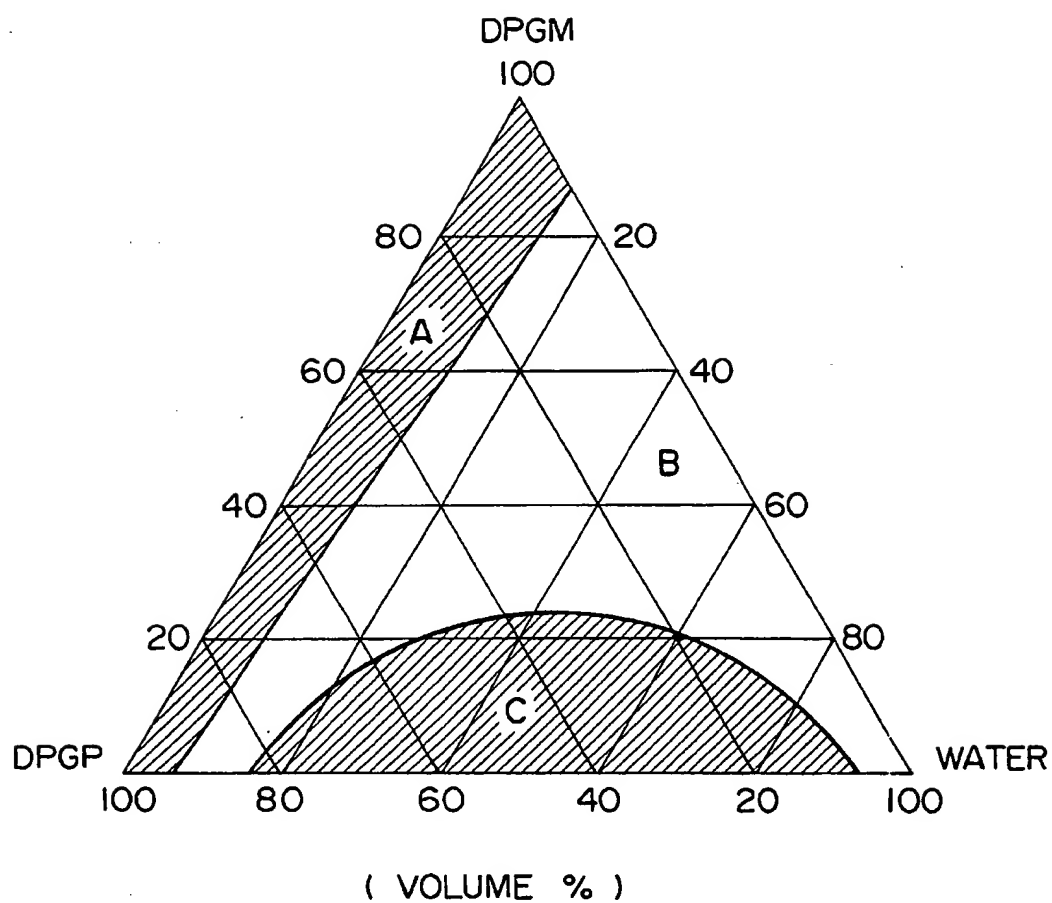
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Primary Examiner—Paul Lieberman*Assistant Examiner*—Michael P. Tierney*Attorney, Agent, or Firm*—Wenderoth, Lind & Ponack[57] **ABSTRACT**

A cleaning agent comprising a mixture of a propylene glycol alkyl ether compatible with water any ratio, a propylene glycol alkyl ether compatible with water only at ratios of 50% by volume or less, and water, for example, the mixture having such a composition that each of 15% by volume or more of dipropylene glycol monomethyl ether, 10% by volume or more of dipropylene glycol monopropyl ether, and 15% by volume or more of water is uniformly dissolved in the other two components. This cleaning agent has high detergency on oily matter, has a characteristic that it is easy to separate the oily matter because the oily matter is not dissolved in the cleaning agent, and is low toxic.

7 Claims, 1 Drawing Sheet



CLEANING AGENT FOR REMOVING FATS AND OILS FROM METAL SURFACES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a cleaning agent for removing foulings such as fats and oils adhering to metal parts, etc. and fluxes and fingerprints adhering to electronic parts, etc., and a cleaning method.

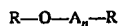
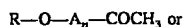
2. Description of the Prior Art

Freon solvents or halogenous solvents have been used for degreasing and cleaning matter to be cleaned such as metal parts, electronic parts, semiconductor parts, etc., chiefly because they are noncombustible and free of danger of ignition, and excellent in detergency. However, in recent years, under concern over the problem of destruction of the earth environment and influence on human bodies, conversion to aqueous cleaning agents containing surface active agents or alkalis as main components, hydrocarbonic cleaning agents, alcoholic cleaning agents, or quasi-aqueous cleaning agents wherein the third petroleum hydrocarbons are dispersed in water using surface active agents is being made.

However, in the case of cleaning methods using aqueous cleaning agents, there are problems that the cleaning agents have too high foamability, are insufficient in detergency, and corrode matter to be cleaned, and a large amount of waste water must be treated, and so on. Both hydrocarbonic cleaning agents and alcoholic cleaning agents are combustible, have high inflammability, and have the danger of ignition. Further, the quasi-aqueous cleaning agents have drawbacks that when phase separation takes place they have inflammability, nonuniformity arises in detergency, and a large amount of waste water must be treated, and so on.

A cleaning agent containing an alkylene glycol monophenyl ether, a glycol ether solvent and a surface active agent as main components is proposed in Japanese Laid-Open Patent Publication No. 51599/1993. However, this cleaning agent does not have sufficient detergency, and there is the possibility that since it contains nonvolatile components, they remain in the matter to be cleaned and have an influence thereon. Further, the growth and reproduction of organisms are influenced by ethylene glycol alkyl ether compounds, and their permissible concentrations are being strictly restricted, and the use thereof is not desirable.

Japanese Laid-Open Patent Publication No. 9498/1993 discloses a cleaning method comprising using composition which comprises a compound represented by the following formula



wherein R is a hydrogen atom or a lower alkyl group, A is an ethoxy or propoxy group, and n is 1 or 2, and water. However, specifically, a cleaning method is disclosed wherein as specific compounds to be used, compounds which dissolve in water at certain temperatures or more, but do not dissolve in water at temperatures lower than the certain temperatures, such as acetates, from propylene glycol monomethyl ether acetate down, and ethylene glycol diethyl ether are used, and their solubility dependent on temperature is utilized.

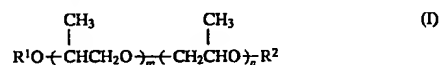
Therefore, there still exists a need for the provision of a cleaning agent which is rich in detergency on oily matter adhering to matter to be cleaned, easy to handle because there is no need of using it under specified temperatures, and further, safer from an ecological viewpoint.

SUMMARY OF THE INVENTION

The present inventors have vigorously studied on detergency of various propylene glycol alkyl ethers, under consideration of using propylene glycol alkyl ethers having less toxicity and higher safety than ethylene glycol alkyl ethers. As a result, they found that certain water sparingly soluble propylene glycol alkyl ethers have high detergency but also have inflammability, and on the other hand, certain water easily soluble propylene glycol alkyl ethers do not have inflammability when mixed with water, but there is a problem in their detergency.

As a result of the above finding, the present inventors have developed a cleaning agent excellent in detergency by mixing the above propylene glycol alkyl ether which has excellent detergency but is water sparingly soluble, the propylene glycol alkyl ether which does not exhibit enough detergency when used alone, but is water easily soluble, and water in an amount enough to lose inflammability. Thus, there is provided according to this invention a cleaning agent which comprises

(A) at least one water easily soluble propylene glycol alkyl ether represented by the formula (I)



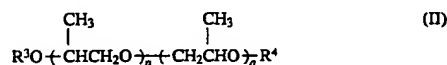
wherein

R¹ and R² are, independently, hydrogen atoms, methyl groups or ethyl groups,

m and n are, independently, 0 or an integer of 1 to 3, and m+n is 1 to 3, provided that one of R¹ and R² is a group other than a hydrogen atom, and

when both R¹ and R² are groups other than hydrogen atoms, both these substituents are methyl groups, and m is 1 and n is 0,

(B) at least one water sparingly soluble propylene glycol alkyl ether represented by the formula (II)



wherein

R³ and R⁴ are, independently, hydrogen atoms, C₁₋₄ alkyl groups,

p and q are, independently, 0 or an integer of 1 to 3, and p+q is 1 to 3, provided that one of R³ and R⁴ is a group other than a hydrogen atom, and

when one of R³ and R⁴ is a hydrogen atom, the other substituent is an alkyl group of C₃ or more,

when R³ and R⁴ are, independently, methyl or ethyl groups, p+q is an integer of 2 or more, and

(C) water, and forms a single phase wherein each component is dissolved in the other components.

Further, a method for cleaning matter to be cleaned, for example, metal pieces, electronic parts or semiconductor parts or the like, on which fats and oils adhered, which method comprises using the above cleaning agent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is the phase diagram of dipropylene glycol monomethyl ether-dipropylene glycol monopropyl ether-water. In the diagram,

A is a region where each of the three components uniformly dissolves in the other components, but the solution has its flash point,

B is a region where each of the three components uniformly dissolves in the other components, and the solution has no flash point, and

C is a region where each of the three components does not uniformly dissolve in the other components.

DETAILED DESCRIPTION OF THE INVENTION

As stated above, the cleaning agent provided by this invention a mixed solution of a water easily soluble propylene glycol alkyl ether classified in (A), a water sparingly soluble propylene glycol alkyl ether classified in (B), and water of (C). This cleaning agent can contain other solvents in common use, so long as its detergency is badly influenced by them.

The term "water easily soluble" herein is used as a concept of using it as a measure that one of the component and water can freely dissolve in the other, at 60° C., in any mutual ratios, and to the contrary, the term "water sparingly soluble" is used as a concept of using it as a measure that one of the component and water can dissolve in the other, at 60° C., only in ratios of the component to water of 50% by volume or less, but these terms are not strictly restricted by the above-mentioned solubilities. Therefore, all of the compounds represented by the above formula (I) can be mentioned as components included in the former, and all of the compounds represented by the above formula (IT) can be mentioned as components included in the latter.

The compound of the formula (I) constituting the component (A) is monomethyl, monoethyl or dimethyl ether of propylene glycol (or 1,2-propanediol), dipropylene glycol (or bis(2-hydroxypropyl)ether) or tripropylene glycol, as understood from the definition. The propylene glycol alkyl ether as the component (A) has an action of enhancing compatibility between the later-described component (B) and water of (C), although it is not limited by the action mechanism. Such propylene glycol alkyl ethers include propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monoethyl ether, propylene glycol dimethyl ether, etc. and mixtures of two or more of them.

The compound of the formula (II) constituting the component (B) is water sparingly soluble, compared with the compounds of the formula (I). Thus, the compound classified herein, when it is a monoalkylether of the above propylene glycol, dipropylene glycol or tripropylene glycol, needs to be an ether having as its alkyl group (R^3 or R^4) a group selected from the group consisting of alkyl groups of C_3 or more, for example, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert.-butyl groups. Further, when R^3 and R^4 in the formula (II) are independently methyl or ethyl groups, the compound classified herein needs to be a dialkyl ether of dipropylene glycol or tripropylene glycol, wherein $p+q$ are 2 or more. Propyl and butyl, herein, mean n-alkyl groups, unless otherwise particularly defined.

The propylene glycol alkyl ether as the component (B) is chiefly a component exhibiting detergency, although it is not

limited by the action mechanism. Such propylene glycol alkyl ethers include propylene glycol monopropyl ether, dipropylene glycol monopropyl ether, tripropylene glycol monopropyl ether, dipropylene glycol dimethyl ether, tripropylene glycol dimethyl ether, dipropylene glycoldiethyl ether, dipropylene glycol dipropyl ether, etc., and mixtures of 2 or more of them.

When among these components (A) and components (B), those preferably used in this invention in view of detergency on oily matter and drying characteristics are exemplified, there can be mentioned, as the components (A), dipropylene glycol monomethyl ether, propylene glycol monoethyl ether and propylene glycol dimethyl ether, and there can be mentioned, as the components (B), preferably propylene glycol monopropyl ether, dipropylene glycol monopropyl ether and dipropylene glycol dimethyl ether, particularly dipreferably propylene glycol monopropyl ether.

Water as the component (C) seems to be combined with the above components (A) and (B) and act so as to reduce the inflammability of the components (A) and (B).

The combination of propylene glycol monopropyl ether or dipropylene glycol monopropyl ether, particularly the latter as the component (B) with the component (A) and the component (C), i.e., water is preferred from the viewpoint that drying is easy to carry out, while detergency on oily matter is not decreased, and the mixture scarcely exhibits inflammability. In cleaning agents of such combination, a possibility that there arises a problem on inflammability is extremely low, even if the content of water at comparatively low levels is adopted.

The mixing ratio among the component (A), the component (B) and the component (C) is not limited so long as these components can form a single phase wherein each component is dissolved in the other components, because in the case, the objects of this invention can be attained. However, since differences in compatibility are seen depending on the kind of each component, it is preferred that the cleaning agent of this invention comprises 15% by volume or more of the propylene glycol alkyl ether of (A), 10% by volume or more of (B) and 15% by volume or more of (C), respectively based on the whole volume of (A), (B) and (C), in view of giving stability in use and excellent detergency. Since the cleaning agent of this invention contains at least the above components (A), (B) and (C) as indispensable components, the respective upper limits thereof to be contained are under 75% by volume as to the component (A), under 70% by volume as to the component (B), and under 75% by volume as to the component (C).

Although it is preferred that the concentration of the component (B) is as high as possible in order to obtain higher detergency, too high concentrations thereof tend to cause phase separation, and therefore, it is further preferred to make the concentration of the component (B) under 50% by volume, make that of the component (A) 25% by volume or more, and make that of the component (C) 20% by volume or more.

In FIG. 1 is shown the phase diagram of the three components system composed of dipropylene glycol monomethyl ether as the component (A), dipropylene glycol monopropyl ether as the component (B) and water as the component (C). The region C in FIG. 1 is a region where each of the three components does not uniformly dissolve in the other components, and two phases of an oil phase and an aqueous phase are formed. The region A and the region B are regions where each of the three components dissolves in the other components, and a single phase is formed. Further, the

regions where hatching was made are regions where the cleaning agents exhibit high inflammability. Although cleaning agents of any compositions in the above region A and region B are usable in this invention, cleaning agents fall within the region A have inflammability because they have such compositions that the amount of water is as small as under 20% by volume. Therefore, cleaning agents having the compositions of the region B not exhibiting inflammability can be preferably used in this invention. When other components (or compounds) are used as the components (A) and (B), a person skilled in the art will be able to determine the optimum ratio on the combination of the components (A), (B) and (C), by preparing such a phase diagram.

The cleaning agent of this invention can be used, in place of known cleaning agents, in various cleaning steps known per se. Therefore, according to this invention, there is provided a method for cleaning matter to be cleaned, for example, metal pieces, electronic parts and semiconductor parts, to which fats and oils adhere, which method comprises using the above cleaning agent.

This cleaning method can be carried out by contacting matter to be cleaned with the cleaning agent of this invention. As this contact method, there can, representatively, be mentioned a method of immersing the matter to be cleaned in the cleaning agent or a method of showering or spraying the cleaning agent on the matter to be cleaned. It is effective, at this time, to combine a means such as ultrasonic cleaning, vibration or stirring.

Usually, the greater part of the oil removed from the matter to be cleaned does not dissolve in the cleaning agent, and separates as a floating oil or a precipitated oil from the cleaning agent. Therefore, the oil can readily be separated from the cleaning agent by treating the washings by an oil-water separation apparatus or the like. Further, the recovered cleaning agent is not polluted with the oil, and maintains high detergency for a long period. In the cases of usual cleaning agents displaying high detergency by dissolving oil, such as hydrocarbonic solvents, halogenous solvents and propylene glycol alkyl ethers, their detergency on matter to be cleaned is influenced by the concentrations of oils dissolving in the cleaning agents, and therefore, there is a need to separate the cleaning agents and the oils by distillation. However, there is no need therefor about the cleaning agent of this invention, and its high detergency can be maintained.

The cleaning agent of this invention can, of course, be applied to washing vessels for degreasing, and can also be applied to rinsing vessels for rinse following the washing vessels. Further, if matter to be cleaned is dried with adhesion of the cleaning agent of this invention, the agent is readily dried without any bad influence on the matter cleaned. Further, when water is used for the rinse of the matter to be cleaned after cleaning, it is unnecessary to use a large amount of rinsing water, which is different from the cases of aqueous cleaning agents or quasi-aqueous cleaning agents.

Thus, the cleaning agent of this invention is rich in detergency on oily matter on matter to be cleaned; is one such that it is easy to separate the oily matter therefrom because the oily matter washed off from the matter to be cleaned does not dissolve in the cleaning agent; and has a long liquid life. Further, since it is possible to make the cleaning agent non-inflammable by appropriately selecting the compounding amount of water, it can be used safely without explosion-proof equipment, which is needed in cleaning apparatuses using hydrocarbonic cleaning agents or alcoholic cleaning agents.

This invention is specifically described below by examples, but not limited thereto.

EXAMPLES 1 TO 14 AND COMPARATIVE EXAMPLES 1 TO 4

Test pieces were prepared by making a commercial machine oil adhere on aluminum sheets of 50 mm×80 mm×1 mm in an amount of about 50 mg/sheet, and 1L portions of cleaning agents of a uniform phase having the compositions shown in Table 1 were used, for cleaning. Cleaning was carried out by immersing the test pieces for 2 minutes in the cleaning agents of cleaning temperatures shown in Table 1, respectively. After the cleaning, the test pieces were drawn up, rinsed with running water for 1 minute, and dried at 80° C. for 20 minutes, and oily matter removal ratios were evaluated on the respective test pieces according to the weight method.

The above procedure was repeated 100 times, the floating oils in the cleaning agents were removed, and oily matter remaining in the cleaning agents was analyzed by the n-hexane method. The second cleaning was carried out under the same conditions as above using the resultant cleaning agents.

The resultant oily matter removal ratios are shown in Table 1.

Further, the flash points of these cleaning agents were measured according to JIS K-2265 Test Method for Measuring Flash Points of Crude Oil and Petroleum Products, and the results are shown in Table 1, too. The measuring method of JIS K-2265 can be outlined as follows.

The following procedure is carried out using a Cleveland open-cup flash point tester.

- ① A sample is filled into an oil cup up to the marked line (about 80 cc).
- ② The test flame nozzle is ignited.
- ③ The sample is heated (heated at the rate of 15° C./min up to about 60° C., and thereafter at the rate of about 5° C./min).
- ④ At 60° C. or more, the test flame is horizontally passed over the oil cup for about 1 second so as to pass at the center of the oil cup, every time the reading of the thermometer rises by 2° C. At that time, it is observed by visual observation if inflammation takes place, and when inflammation takes place, its lowest temperature is recorded.

The meanings of the abbreviations in the table are as follows. The values in the parentheses are solubilities in water at 60° C.

Component (A)

DPM: Dipropylene glycol monomethyl ether

TPM: Tripropylene glycol monomethyl ether

PE: Propylene glycol monoethyl ether

PDM: Propylene glycol dimethyl ether

Component (B)

PP: Propylene glycol monopropyl ether (28% by volume)

DPP: Dipropylene glycol monopropyl ether (10% by volume)

PB: Propylene glycol monobutyl ether (6% by volume)

DPDM: Dipropylene glycol dimethyl ether (36% by volume)

TPDM: Tripropylene glycol dimethyl ether (24% by volume)

DPDE: Dipropylene glycol diethyl ether (5% by volume)

DPB: Dipropylene glycol monobutyl ether (5% by volume)

TPB: Tripropylene glycol monobutyl ether (2% by volume)

Other components

EPh: Ethylene glycol monophenyl ether (2% by volume)

TABLE I

Composiuion (V/V %)												
No.	A					B						Water
	DPM,	TPM,	PE,	DPE,	PDM	PP,	DPP,	DPDM,	TPDM,	DPDE,	DPPM	
Example												
1	20					20						60
2	15						10					75
3	20						60					20
4	25						10					65
5	25						50					25
6	30						40					30
7	20							65				15
8	35								35			30
9	50									30		20
10	50										30	20
11		50					20					30
12			25					30				45
13					50		20		20			30
14												30
Comparative example												
1			70									30
2	70											30
3						15						85
4							12					88

No.	Flash point (°C.)	Cleaning temperature (°C.)	Oil removal ratio (%)		Oil concentration in the cleaning agent (W %)
			1st time	2nd time	
Example					
1	not inflamed	50	85	85	0.2
2	not inflamed	40	88	85	0.1
3	not inflamed	50	98	99	1.2
4	not inflamed	50	90	88	0.1
5	not inflamed	40	97	95	1.0
6	not inflamed	40	95	96	0.8
7	not inflamed	60	93	95	1.0
8	not inflamed	60	93	93	0.2
9	not inflamed	60	95	85	0.2
10	not inflamed	60	92	93	0.3
11	not inflamed	50	90	90	0.1
12	not inflamed	50	92	92	0.5
13	not inflamed	50	90	90	0.2
14	not inflamed	60	88	89	0.1
Comparative example					
1	72	60	65	65	under 0.1
2	not inflamed	60	67	65	under 0.1
3	not inflamed	60	54	50	under 0.1
4	not inflamed	60	50	50	under 0.1

EXAMPLES 15 and 16

Comparison between DPP and PB as the component (B) (in view of inflammability)

The process of Examples 1 to 14 was repeated on cleaning agents having the compositions shown in the following Table 2. The results are shown together in Table 2.

TABLE 2

Example No.	Composition (V/V %)				Flash point (°C.)	Oil removal ratio (%)
	A	B		C		
	DPM	PB	DDP	Water		
3	20		60	20	not inflamed	98
15	20	60		20	92	—
16	30	40		30	not inflamed	95

*Cleaning temperature: 50° C.

Although the flash point of PB is 62° C., it is possible, in the three components system of this invention, to greatly raise flash point, but nevertheless the composition having the low water content still has inflammability. This means that when PB having relatively high inflammability is used, there is a need to increase the amount of water, and on the other hand, in order to ensure compatibility, there is a need to increase the amount of the component (A), too. Therefore, when characteristics on inflammability equal to the system wherein DPP was used are desired, the lowering of the oil removal ratio is unavoidable.

EXAMPLES 17 TO 19

Comparison among DPP, DPB and TPB as the component (B) (in view of compatibility)

Compositions exhibiting compatibility at 50° C., shown in the following Table 3 were prepared. Since DPB and TPB have only low solubilities in water, there was a need to make the amount of the component (A) relatively large, for obtaining a single phase. The oil removal test was carried out according to the method described in the preceding examples. The results are shown together in Table 3.

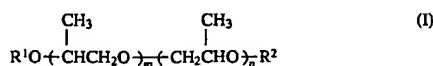
TABLE 3

Example No.	Composition (V/V %)					Oil removal ratio (%)
	C	DPP	DPB	TPB	A	
	Water				DPM	
17	20	65			15	99
18	20		50		30	93
19	20			40	40	92

What is claimed is:

1. A cleaning agent for removing fats and oils adhered to metal pieces, electronic parts or semiconductor parts which comprises the following components:

(A) at least one water easily soluble propylene glycol alkyl ether represented by the formula (I)



wherein

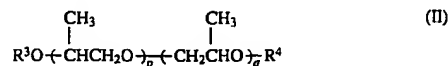
R¹ and R² are, independently, hydrogen atoms, methyl groups or ethyl groups,

m and n are, independently, 0 or an integer of 1 to 3, and

m+n is 1 to 3, provided that, one of R¹ and R² is a group other than a hydrogen atom, and

when both R¹ and R² are groups other than hydrogen atoms, both these substituents are methyl groups, and m is 1 and n is 0,

(B) at least one water sparingly soluble propylene glycol alkyl ether represented by the formula (II)



wherein

R³ and R⁴ are, independently, hydrogen atoms, C₁₋₄ alkyl groups,

p and q are, independently, 0 or an integer of 1 to 3, and

p+q is 1 to 3, provided that one of R³ and R⁴ is a group other than a hydrogen atom, and

when one of R³ and R⁴ is a hydrogen atom, the other substituent is an alkyl group of C₃ or more,

when R³ and R⁴ are independently, methyl or ethyl groups, p+q is an integer of 2 or more, and

(C) water;

said cleaning agent forming a single phase wherein the propylene glycol ether (A) is present in amounts of 25% or more by volume, the propylene glycol alkyl ether (B) is present in amounts of 20% or more by volume and, the water (C) is present in amounts of 20% or more by volume, respectively, based on the whole volume of the cleaning agent.

2. The cleaning agent of claim 1 wherein the propylene glycol alkyl ether of (A) is one or more ethers selected from the group consisting of propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monoethyl ether and propylene glycol dimethyl ether.

3. The cleaning agent of claim 1 wherein the propylene glycol alkyl ether of (B) is one or more ethers selected from the group consisting of propylene glycol monopropyl ether, dipropylene glycol monopropyl ether, tripropylene glycol monopropyl ether, dipropylene glycol dimethyl ether, tripropylene glycol dimethyl ether, dipropylene glycol diethyl ether and dipropylene glycol dipropyl ether.

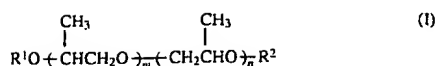
4. The cleaning agent of claim 1 wherein the propylene glycol alkyl ether of (A) is selected from the group consisting of dipropylene glycol monomethyl ether, propylene glycol monoethyl ether and propylene glycol dimethylether, and the propylene glycol alkyl ether of (B) is selected from the group consisting of propylene glycol monopropyl ether, dipropylene glycol monopropyl ether and dipropylene glycol dimethyl ether.

5. The cleaning agent of claim 1 wherein the propylene glycol alkyl ether of (A) is selected from the group consisting of dipropylene glycol monomethyl ether, propylene glycol monoethyl ether and propylene glycol dimethyl ether, and the propylene glycol alkyl ether of (B) is dipropylene glycol monopropyl ether.

6. A process for cleaning metal pieces, electronic parts or semiconductor parts to which fat and oil adhered, which comprises

(a) a step of preparing a cleaning agent which comprises 25% by volume or more per the whole volume of the cleaning agent of (A) at least one water easily soluble propylene glycol alkyl ether represented by the formula (I)

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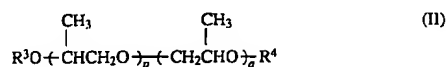
wherein

R¹ and R² are, independently, hydrogen atoms, methyl groups or ethyl groups,

m and n are, independently, 0 or an integer of 1 to 3, and m+n is 1 to 3, provided that one of R¹ and R² is a group other than a hydrogen atom, and

when both R¹ and R² are groups other than hydrogen atoms, both these substituents are methyl groups, and m is 1 and n is 0,

20% by volume or more per the whole volume of the cleaning agent of (B) at least one water sparingly soluble propylene glycol alkyl ether represented by the formula (TT)



wherein

R³ and R⁴ are, independently, hydrogen atoms, C₁₋₄ alkyl groups,

p and q are, independently, 0 or an integer of 1 to 3, and p+q is 1 to 3, provided that one of R³ and R⁴ is a group other than a hydrogen atom, and

when one of R³ and R⁴ is a hydrogen atom, the other substituent is an alkyl group of C₃ or more,

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when R³ and R⁴ are, independently, methyl or ethyl groups, p+q is an integer of 2 or more, and

one of R³ and R⁴ is a group other than a hydrogen atom, and

15% by volume or more per the whole volume of the cleaning agent of (C) water, and forms a single phase wherein each component is dissolved in the other components, and

(b) a step of immersing the above matter to be cleaned on which fat and oil adhered in the cleaning agent, or showering or spraying the cleaning agent on the matter to be cleaned.

7. The cleaning process of claim 6 wherein the propylene glycol alkyl ether of (A) in the cleaning agent is selected from the group consisting of propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monoethyl ether and propylene glycol dimethyl ether, and the propylene glycol alkyl ether of (B) is selected from the group consisting of propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monopropyl ether, tripropylene glycol monopropyl ether, dipropylene glycol dimethyl ether, tripropylene glycol dimethyl ether, dipropylene glycol diethyl ether and dipropylene glycol dipropyl ether.

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(71) Applicant: **ETHYL PETROLEUM ADDITIVES LIMITED**

Bracknell, Berkshire RG12 2UW (GB)

(72) Inventors:

• **Poat, Julia C.**

Bracknell, Berkshire, RG12 9PS (GB)

• **Walters, David K.**

Camberley, Surrey, GU17 7TR (GB)

• **MacPherson, Ian**

Richmond, Virginia 23233 (US)

(74) Representative: **Cresswell, Thomas Anthony**

J.A. KEMP & CO.

14 South Square

Gray's Inn

London WC1R 5LX (GB)

(54) Friction modification of synthetic gear oils

(57) Gear lubricant compositions having a kinematic viscosity at 100°C in the range of 4 to 32 mm².s⁻¹ (cSt), and comprise (a) a base oil having (i) more than 20% by volume of hydrogenated poly- α -olefin oil and (ii) less than 80% by volume of mineral oil or synthetic ester oil or a combination thereof; (b) an amount of an additive package such that the lubricant satisfies or exceeds the specifications for API GL-4 service; and (c) a friction improving amount in the range of 0.01 to 2 wt% based on the total weight of the lubricant of at least one over-based alkaline earth metal sulphurised phenate or salicylate, the lubricant being essentially free of any metal additive component other than said phenate or salicylate, and has on a weight basis a boron content, if any, of not more than 1,000 ppm.

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Description

This invention relates to improving the frictional characteristics of gear oils in which the base oil is, or contains a substantial quantity of a synthetic poly-alpha-olefin oil (PAO).

5 PAOs possess good thermal stability and viscometric properties. However attempts to formulate PAO-based gear oils especially transmission oils for use in large vehicles equipped with manual transmissions of the synchronizer type pose special problems. Even though such lubricants contain additives for wear protection, corrosion protection, and other property improvements, the lubricants afford unsuitably low frictional properties in synchronizer-based transmissions and thus cause poor synchronization of the gear changes. This negative aspect of such synthetic based gear oils is readily observed as low friction and noisy gear change in the Zahnradfabrik Friedrichshafen A.G. synchronizer test (described and referred to hereinafter as the "ZF Synchronizer test").

It has now been found possible to overcome this problem by means of small amounts of an additive which does not materially affect the other performance capabilities of the finished lubricant.

15 The additives used pursuant to this invention are overbased alkaline earth metal salts of oil-soluble sulfurized phenols or oil-soluble salicylic acids. The metals of such salts preferably are those which have low toxicity and which present little or no concern from the environmental standpoint, namely, magnesium and calcium. However, the overbased barium and strontium salts can be used, if desired.

In accordance with one embodiment of this invention, there is provided a lubricant having a kinematic viscosity at 100°C in the range of 4 to 32 mm².s⁻¹ (cSt), and preferably in the range of 8 to 20 mm².s⁻¹ (cSt), and comprising:

- 20 a) a base oil having (i) more than 20% by volume of hydrogenated poly-alpha-olefin oil and (ii) less than 80% by volume of mineral oil or synthetic ester oil or a combination thereof;
- b) an amount of a gear oil additive package such that the lubricant satisfies or exceeds the specifications for API GL-4 service; and
- 25 c) a friction improving amount in the range of about 0.01 to about 2 wt % based on the total weight of the lubricant of at least one overbased alkaline earth metal sulfurized phenate or salicylate;

said lubricant being essentially free of any metal additive component (i.e., the lubricant contains at most 100 ppm and preferably no more than 50 ppm of metal as one or more additive components other than said phenate or salicylate), and having on a weight basis a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm. In one embodiment the lubricant has no boron additive content. In preferred embodiments the lubricant contains no metal additive component other than said phenate or salicylate.

30 Preferably the base oil of the above gear lubricant is composed of (i) at least 40%, and more preferably least 50%, by weight of hydrogenated poly-alpha-olefin oil; (ii) 5 to 25% by weight of synthetic ester oil, and (iii) 0 to 55%, and more preferably 0 to 50% by weight of mineral oil. It will be seen that the mineral oil is an optional component of the base oil.

Additional embodiments comprise use of the above lubricants in manual transmissions of the synchronizer type to improve the performance of the transmission during operation under service conditions. The lubricants can also be used to lubricate the axle or differential gearing system of the vehicle.

40 In the ZF Synchronizer test the beneficial increase in friction exhibited by finished gear lubricants of this invention manifests itself in a substantial increase in the number of cycles during which the test can be performed without poor synchronization of the gear changes and/or with the coefficient of friction being greater than 0.065.

In satisfying or exceeding the specification for API GL-4 service, the finished lubricant satisfies the requirements for other performance specifications such as API GL-5, and including specifications not yet in being (or even envisioned) such as MT-1, PG2, API GL-7, and MIL-L-2105E or specifications of other countries such as comparable JIS gear oil standards, or the like. In other words the specifications of API GL-4 are to be considered minimum performance levels which the gear oil additive package (b) imparts to the finished lubricant. For example, if the requirements of the API GL-7 specification are more stringent than API GL-4, an additive package that provides a lubricant which satisfies the API GL-7 requirements inherently satisfies the minimum performance requirements for use in the practice of this invention, whether or not the package has actually been subjected to the API GL-4 performance tests.

50 Another embodiment of this invention comprises the use of at least one overbased alkaline earth metal sulfurized phenate or salicylate in a gear lubricant composed of components a) and b) above -- especially a manual transmission lubricant for use in vehicles equipped with manual transmissions of the synchronizer type -- to improve the frictional properties of the lubricant without materially affecting the other performance capabilities of the finished lubricant, wherein, as described above, the lubricant is essentially free of any metal additive component other than the overbased phenate or salicylate, and has a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm.

Still another embodiment is a gear oil additive package which comprises (1) an oil-soluble phosphorus and sulfur-containing antiwear and/or extreme pressure additive complement and (2) at least one overbased alkaline earth metal sulfurized phenate or salicylate; said gear oil additive package being further characterized in that when blended with a

base oil having a kinematic viscosity in the range of 4 to 32 cSt at 100°C and composed of a base oil as described above to form a lubricant containing from about 0.01 to about 2 wt % of said phenate or salicylate, the gear oil additive package provides a lubricant composition that:

- A) satisfies or exceeds the specifications for API GL-4 service;
- B) contains, if any, at most 100 ppm and preferably no more than 50 ppm of metal apart from the metal content of said phenate or salicylate; and
- C) has a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm.

In another embodiment, a gear oil additive package (concentrate) or gear lubricant of this invention additionally contains at least one oil-soluble basic nitrogen-containing ashless dispersant, preferably a succinimide ashless dispersant and/or a succinic ester-amide ashless dispersant, and more preferably a Mannich base ashless dispersant. The oil-soluble phosphorus and sulfur-containing antiwear and/or extreme pressure additive complement of such compositions is preferably composed of (1) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent in which the sulfur is bonded to carbon or to more sulfur, and (2) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent. In these embodiments, the dispersant and the metal-free sulphur-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of about 0.0005:1 to about 0.5:1, and preferably in the range of about 0.003:1 to about 0.2:1. Likewise the dispersant and the metal-free phosphorus-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of about 0.005:1 to about 5:1, and preferably in the range of about 0.01:1 to about 2:1. In each of these embodiments the gear oil additive package (concentrate) or gear lubricant preferably has a boron content such that the finished lubricant contains by weight up to 1,000 ppm, preferably up to 300 ppm, and most preferably not more than 25 ppm of boron. One preferred way of introducing at least a portion of such boron is to provide additive packages and finished lubricants compositions containing a borated basic nitrogen-containing ashless dispersant.

In additional embodiments, any of the above additive concentrates and finished lubricant compositions further comprise at least one oil-soluble demulsifying agent.

Preferably the lubricant compositions of this invention have a halogen content, if any, of no more than 100 ppm, and more preferably no more than 50 ppm on a weight basis.

Still another aspect of this invention is the method of beneficially modifying the frictional characteristics of a low-friction synthetic lubricant composition containing a gear oil additive package such that the lubricant composition satisfies or exceeds the specifications for API GL-4 service, but does not exhibit satisfactory friction properties for use in manual transmissions, particularly those of the synchronizer type. The method comprises including in such lubricant composition an amount in the range of about 0.01 to about 2 wt % based on the total weight of the lubricant of at least overbased sulfurized phenate or salicylate such that the friction properties of the lubricant are improved for use in manual transmissions, particularly those of the synchronizer type.

In each of the embodiments of this invention, the overbased metal phenate or salicylate can be employed as a separate component (e.g., as a "top-treat" to the base oil with which the additive package has been or will be blended) or as a component of the additive package itself. Similarly, while use of additive packages is preferred, it is possible to blend the overbased metal sulfurized phenate and/or salicylate and the respective components of the additive package into the base oil individually or in various compatible sub-combinations.

Base Oils.

Most poly-alpha-olefin oils are formed by oligomerization or co-oligomerization of 1-alkene hydrocarbon having 6 to 20 and preferably 8 to 16 carbon atoms in the molecule and hydrogenation of the resultant oligomer. In some cases, a suitable poly-alpha-olefin oils can be co-oligomers of a short chain 1-olefin such as ethylene and one or more longer chain alpha-olefins, such as for example the product available from Mitsui Petrochemical Company, Ltd. under the LUCANT trademark. Hydrogenated poly-alpha-olefin oils formed from 1-decene are particularly preferred. Methods for the production of liquid 1-alkene hydrocarbon oils are known and reported in the literature. See for example U. S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822.

Synthetic ester oils are available in the marketplace. Typical synthetic ester oils include such materials as the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(1-ethylpropyl) adipate, di(1,3-dimethylbutyl) adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate,

dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, di(1-methylpropyl) azelate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, mixed C₉ and C₁₁ dialkyl phthalate, dibutyl sebacate, di(1-ethylpropyl) sebacate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Other synthetic esters which may be used as synthetic oils include those made from C₃-C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylol propane tripelargonate and pentaerythritol tetracaproate serve as examples.

The base oils may contain as optional blending components a mineral oil or other suitable oleaginous liquid of lubricating viscosity, provided the overall base lubricant satisfies the proportions and viscosity parameters given above, and is suitable for use in forming a finished gear lubricant that satisfies or exceeds the specifications for API GL-4 service, and provided further that the resultant finished oil remains amenable to friction improvement pursuant to this invention. Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, hydrotreated oils, partially hydrotreated oils, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques known to those skilled in the art. Suitable reprocessed or reclaimed mineral oil base stocks may also be used. Most gear oil packages contain diluent oils or solvents for certain active ingredients or components. However, since such diluent oils or solvents are added to the base oil along with the additive package or with one or more additive components blended separately or individually into the base oil, such diluent oils or solvents are to be omitted from consideration when assessing the makeup of the base oil of the compositions of this invention.

Overbased Phenate or Salicylate

Overbased alkaline earth metal sulfurized phenates are also known as overbased alkaline earth metal phenol sulfides. These materials as well as overbased alkaline earth metal salicylates are available as articles of commerce. Of the overbased alkaline earth phenates and salicylates, the magnesium compounds are a preferred group. The most preferred however are the overbased calcium phenates and salicylates. As between overbased phenates and overbased salicylates, the phenates are preferred. As is known, these overbased materials contain more than a stoichiometric amount of the metal. Methods for producing such materials have been reported in the patent literature. Test work has shown that the additive must be overbased, and for good performance the phenate should have a total base number (TBN) of at least 200 and preferably at least about 250. The salicylate should have a TBN of at least 150. TBN is measured using the ASTM D2896 procedure, and represents mg of KOH per gram of sample.

Quantities ranging from as little as 0.01 wt% up to as much as 2 wt% of the overbased metal phenate or salicylate (or combination thereof) based on the total weight of the finished lubricant can be employed. Ordinarily the amount used will not be greatly in excess of that amount needed to yield the friction performance desired in the particular finished gear oil lubricant in question. In most cases the amount will not be above 1 wt%, and often will not exceed 0.5 wt%. In the case of the friction-improved additive packages of this invention, the amount will be proportioned such that when the package is blended into the base oil at the recommended, or desired concentration, the resultant finished oil will contain the above-specified amount of the overbased phenate or salicylate. These proportions of the overbased metal phenate or salicylate are based on the active ingredient, and thus the weight of any solvent or diluent associated with the overbased phenate or salicylate as used should be subtracted from the additive weight when calculating the concentration of the overbased metal phenate or salicylate in the finished oil or in the friction-improved additive package. However the total weight of the finished oil or of the completed additive package will include the weight of such solvent or diluent.

Additive Packages

The specifications for API GL-4 and API GL-5 service are published in ASTM Publication STP-512A entitled "Laboratory Performance Tests for Automotive Gear Lubricants" (March 1987).

A number of gear oil additive packages (concentrates) that provide API GL-4 or API GL-5 performance are available in the marketplace. They generally contain at least a sulfur-phosphorus antiwear or extreme pressure additive system, one or more antioxidants, one or more corrosion inhibitors, and an antifoam additive and may, preferably do, contain a dispersant additive.

ZF Synchronizer Test

As is known in the art, the ZF Synchronizer test has been designed for the evaluation of oil performance in com-

mercially available synchromesh units under endurance conditions with the bulk lubricant temperature controlled at a relatively high level. While it is important to simulate fairly closely the actual conditions met in service, the need to produce a test result in an acceptable period has to be taken into account. Briefly, two halves of a transmission synchromesh unit are repeatedly brought together under conditions of known force and speed differential until failure occurs.

Failure may be defined in terms of synchromesh performance or overall wear. The test rig used in the procedure was designed with consideration of work done by Socin and Walters, SAE Paper Number 680008 entitled "Manual Transmission Synchronizers"; Fano, CEC TLPG4 Chairman's Final Report, 1985, entitled "Synchromesh Test Method With Proposed Synchro Test Rig"; and Brugen, Thies and Naurian of Zahnradfabrik Friedrichshafen A.G. in a paper entitled "Einfluss Des Schmierstoffes auf die Schaltelelemente Von Fahrzeuggetrieben". The two synchromesh units are assembled in a gear box which forms the oil reservoir and facilitates splash lubrication of components. Drive may be transmitted along the main shaft or via the layshaft gears to give an increased ratio. The input speed is kept constant by means of a DC drive control system and a large flywheel simulating vehicle inertia. On changing gear, the output shaft accelerates and decelerates the small flywheel which simulates clutch inertia. A pivot linkage connected to a pneumatic cylinder provides the actuating force which is measured by means of a load ring strain gauge. A small heater is used to control oil temperature.

Torque transmitted through the output shaft can be measured to give an indication of the coefficient of friction between the synchronizing cones. The synchromesh units used are standard commercially available steel units with a molybdenum-based plasma spray coating on the inner surface of the outer synchro-ring. The synchromesh units are renewed before each test. Typically, when measured at a point of relatively high torque during a gear change, the coefficient of friction for satisfactory synchronizer performance in the test is at least 0.065.

Another performance criterion which may be used when performing the test for qualification purposes is excessive vibration of the gear box casing in the axial plane, a condition symptomatic of poor gear changes. For this purpose the control and monitoring of the rig is coordinated by a process controller. During a test the number of poor changes is recorded. The test is terminated prematurely if this number becomes unacceptable or the vibration becomes excessively harsh.

Test components may be evaluated by inspecting the friction surface of the inner synchronizer cone using a Perthometer stylus device both before and after test. Polishing of the metal surface or the build up of a glaze of decomposed lubricant or additive yields an unacceptably smooth surface finish. This in turn causes low frictional values during the gear change and can lead to clash of the sleeve and gear clutch teeth. Wear measurements are also made on the test components.

Performance

The following examples illustrate, inter alia, the dramatic improvements in performance that are made possible by the practice of this invention. These examples are not intended to limit, and should not be construed as limiting, this invention. In the examples, all percentages are by weight.

Example

ZF Synchronizer tests were performed under the same conditions using a lubricant of this invention and a control lubricant made from the same components with but one exception: the composition of this invention contained 0.5% (approximately 0.3% on an active ingredient basis) of an overbased calcium sulfurized alkyl phenate having a nominal TBN of 250 ("Phenate"), whereas the control contained no such component. The base oils were fully synthetic oil blends of two PAO fluids having nominal viscosities at 100°C of 8 and 40 cSt ($\text{mm}^2 \cdot \text{s}^{-1}$), and a synthetic ester, namely bis(tridecyl)-adipate ("DTDA"). Each lubricant contained the same quantity of the same metal-free and boron-free API GL-4 additive package (HiTEC 381, available from Ethyl Corporation). The proportions of these components are summarised in the following table:

Components	Control Composition, %	Invention Composition, %
PAO, 8 $\text{mm}^2 \cdot \text{s}^{-1}$	70.25	69.75
PAO, 40 $\text{mm}^2 \cdot \text{s}^{-1}$	16.00	16.00
DTDA	10.00	10.00
API GL-4 Package	3.75	3.75
Phenate	None	0.50

The control composition had a kinematic viscosity at 100°C of $9.53\text{mm}^2\cdot\text{s}^{-1}$. The composition of the invention had a kinematic viscosity at 100°C of $9.55\text{mm}^2\cdot\text{s}^{-1}$.

The control composition was able to complete only 792 cycles in the test. The test had to be shut down at that point because very harsh bad gear changes had occurred and the coefficient of friction had already fallen to below 0.05. In sharp contrast, the composition of this invention successfully completed 50,000 cycles, and during the entire test the coefficient of friction remained consistently above 0.065.

Claims

1. A lubricant having a kinematic viscosity at 100°C in the range of 4 to $32\text{mm}^2\cdot\text{s}^{-1}$ (cSt), and comprising:
 - a) a base oil comprising (i) more than 20% by volume of hydrogenated poly- α -olefin oil and (ii) less than 80% by volume of mineral oil and/or synthetic ester oil;
 - b) an amount of a gear oil additive package such that the lubricant satisfies or exceeds the specifications for API GL-4 service; and
 - c) a friction improving amount in the range of 0.01 to 2wt% based on the total weight of the lubricant of at least one overbased alkaline earth metal sulphurised phenate or salicylate;
- the lubricant being essentially free of any metal additive component other than the phenate or salicylate, and having on a weight basis a boron content of not more than 1,000 ppm.
2. A lubricant according to claim 1 which does not contain any metal-containing additive component other than the phenate or salicylate, and which has on a weight basis a boron content of not more than 300 ppm.
3. A lubricant according to claim 1 or 2 which has a boron content not more than 25 ppm.
4. A lubricant according to any one of claims 1 to 3 which does not contain boron.
5. A lubricant according to any one of claims 1 to 4 wherein component c) is at least one overbased alkaline earth metal sulphurised phenate having a TBN of at least 200.
6. A lubricant according to claim 5 wherein the phenate is an overbased calcium sulphurised phenate having a nominal TBN of 250.
7. A lubricant according to any one of claims 1 to 6 wherein the base oil a) comprises (i) at least 40% by weight of hydrogenated poly- α -olefin oil; (ii) 5 to 25% by weight of synthetic ester oil, and (iii) 0 to 55% by weight of mineral oil.
8. A lubricant according to any one of claims 1 to 7 wherein the gear oil additive package b) comprises at least one oil-soluble basic nitrogen-containing ashless dispersant and an oil-soluble phosphorus and sulphur-containing antiwear and/or extreme pressure additive complement comprising (1) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent in which the sulphur is bonded to carbon or to more sulphur and (2) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent, wherein the dispersant and the metal-free sulphur-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of 0.0005:1 to 0.5:1, and the dispersant and the metal-free phosphorus-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of 0.005:1 to 5:1.
9. A lubricant according to any one of claims 1 to 8 having on a weight basis a halogen content of no more than 100ppm.
10. Use in a manual transmission of the synchronizer type of a lubricant according to any one of claims 1 to 9 to improve transmission performance during operation under service conditions.
11. Use of at least one overbased alkaline earth metal sulphurised phenate or salicylate to improve the frictional properties of a lubricant comprising a) a base oil as defined in claim 1 or 7 and b) a gear oil additive package as defined

in claim 1, the lubricant being essentially free of any metal additive component other than the phenate or salicylate and having on a weight basis a boron content of not more than 1,000 ppm.

- 5 12. Use according to claim 11, wherein the lubricant comprises from 0.01 to 2 wt% based on the total weight of the lubricant of overbased sulphurised phenate or salicylate.
- 10 13. A gear oil additive concentrate which comprises (1) an oil-soluble phosphorus and sulphur-containing antiwear and/or extreme pressure additive complement and (2) at least one overbased alkaline earth metal sulphurised phenate or salicylate wherein, when blended with a base oil as defined in claim 1 or 7 to form a lubricant containing from 0.01 to 2 wt% of said phenate or salicylate, the gear oil additive concentrate provides a lubricant which has a kinematic viscosity at 100°C in the range of 4 to 32mm².s⁻¹ (cSt), which satisfies or exceeds the specifications for API GL-4 service, which contains up to 100 ppm of metal additive component other than the phenate or salicylate, and which has a boron content of not more than 1,000 ppm.
- 15 14. A gear oil additive concentrate according to claim 13 which when blended with base oil provides a lubricant which contains no metal additive other than the phenate or salicylate, and which has a boron content of not more than 300 ppm.
- 20 15. A gear oil additive concentrate according to claim 13 or 14 additionally comprising at least one oil-soluble basic nitrogen-containing ashless dispersant and in which the oil-soluble phosphorus and sulphur-containing antiwear and/or extreme pressure additive complement of the concentrate comprises (1) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent in which the sulphur is bonded to carbon or to more sulphur, and (2) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent wherein the dispersant and the metal-free sulphur-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of 0.0005:1 to 0.5:1, and the dispersant and the metal-free phosphorus-containing antiwear and/or extreme pressure agent are proportioned such that the mass ratio (wt/wt) of nitrogen in the dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of 0.005:1 to 5:1.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 0983

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-5 250 122 (UCHIDA ET AL.) * examples 3,4; table 1 *	1-6,9	C10M169/04
Y	EP-A-0 578 435 (ETHYL) * the whole document *	1-15	
Y	EP-A-0 501 527 (LUBRIZOL) * page 9, line 1 - line 20; claims 11,12 * * page 17, line 40 - line 45 *	1-15	
Y	EP-A-0 620 268 (ETHYL) * page 2 * * page 3, line 34 - line 40 *	1-15	
A	EP-A-0 531 585 (ETHYL) * the whole document *	1-15	
A	WO-A-87 05927 (LUBRIZOL) * page 5, line 1 - line 10; claims 1,3,6 *	1	
A	US-A-5 089 156 (CHRISOPE ET AL.) * examples 1-47 *	1-15	
			C10M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 October 1996	Examiner De La Morinerie, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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United States Patent [19]

Simpson, Jr.

[11] 4,187,191

[45] Feb. 5, 1980

[54] **PHOTORESIST STRIPPER WITH
DODECYLSULFONIC ACID AND
CHLORINATED SOLVENTS**

[75] Inventor: George W. Simpson, Jr., Cicero, Ind.

[73] Assignee: General Motors Corporation, Detroit,
Mich.

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[58] Field of Search 252/162, 143, 171, 142,
252/558, 549, 554; 134/3, 38, 40, 42

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Primary Examiner—Harris A. Pitlick

Attorney, Agent, or Firm—Robert J. Wallace

[57]

ABSTRACT

A stripper for removing a photoresist mask. The stripper consists essentially, by volume, of about 50–85% tetrachloroethylene and ortho-dichlorobenzene in generally equal amounts, about 15–50% dodecylsulfonic acid, and up to 3% formic acid.

5 Claims, No Drawings

PHOTORESIST STRIPPER WITH DODECYSULFONIC ACID AND CHLORINATED SOLVENTS

BACKGROUND OF THE INVENTION

This invention relates to a photoresist stripper and more particularly to a composition for removing an organic solvent strippable polymer and/or colloid photoresist mask from a face of a silicon wafer.

Various types of polymer and/or colloid materials are used to partially mask surfaces for selective etching of those surfaces. The polymers may be natural or synthetic and are resistant to attack by acids. Such masking materials are frequently referred to as resists. Some resists are photosensitive, so that the masking patterns can be photographically produced on the surface to be protected. These latter resists are normally referred to as photoresists. The process of photographically defining a photoresist mask on a metal surface and then etching away the unprotected portions of the metal surface is generally referred to as photoengraving.

Photoresist maskants are used, for example, to engrave complex decorative patterns on a surface, to engrave plates for printing photographs, to define wiring and connection patterns on electronic circuit boards, and to etch oxide layers and metallization patterns for semiconductor devices such as transistors and integrated circuits. It is obviously highly desirable that the photoresist be adherent and highly resistant to attack by the etchant. This permits deep etches, high resolution patterns, etc. Generally, the more resistant the photoresist is to etchant attack, the more difficult it is to remove.

In making semiconductor devices, it is particularly important that the photoresist be especially resistant to attack and yet especially thoroughly removed after it is used. In semiconductor device manufacture, the photoresist is applied to the face of a semiconductive material wafer. The pattern is photographically delineated, and the wafer face selectively etched. The photoresist must then be meticulously removed to prepare the wafer face for subsequent processing steps. No residue or surface contamination should be left on the wafer face. A typical photoresist used in semiconductor device manufacture is KMER (Kodal Metal Etch Resist). This type of photoresist is an organic solvent strippable polymer and/or colloid of the type disclosed in U.S. Pat. Nos. 2,848,328 Hefner; 2,852,379 Hefner et al; 2,940,853 Sangura et al; and 3,458,313 Webb. Photoresists such as these have been removed in the past using a wide variety of strippers, including chlorinated solvents and oxygenated organic materials such as phenols and cresols. U.S. Pat. Nos. 3,335,087 Koers and 3,335,008 Mandell, Jr. disclose adding hydrofluoric acid to such strippers. Phenol-type and cresol-type materials comprise a substantial proportion of popular commercially available strippers. On the other hand, such strippers have special handling and waste disposal requirements I consider desirable to avoid. Such strippers can be avoided, for example, by using special stripping techniques, as for example by using elevated stripper temperatures and/or pressures.

I have found a stripping composition that does not require a mineral acid or an oxygenated organic solvent. Accordingly, it is less caustic and waste disposal is considerably easier. In addition, my composition is highly miscible with water and does not require any

special temperatures or pressures for use. It can be used under atmospheric pressure at room temperature, which makes handling of the composition considerably easier. It is thorough in its cleansing action, leaving no recognizable residue or surface contamination, and is simple to use. Moreover, it is stable, low in initial cost and in disposal cost, and can even be reclaimed by distillation.

OBJECTS AND SUMMARY OF THE INVENTION

An object of this invention is to provide a new composition for stripping photoresist masks, particularly photoresist masks on a semiconductor wafer face.

The invention comprehends a stripper composition comprising, by volume, about 15-50% dodecylsulfonic acid, up to 3% formic acid, and the balance equal portions of tetrachloroethylene and ortho-dichlorobenzene.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention combines a high proportion of dodecylsulfonic acid with equal volume proportions of two chlorinated organic solvents previously known to be useful in photoresist stripping. The dodecylsulfonic acid provides a stronger and more thorough stripping action and makes the stripper miscible with water. The two organic solvents in my stripper are tetrachloroethylene and ortho-dichlorobenzene. Additions of up to 3%, by volume, formic acid appear to enhance the stripping action even further. However, the enhanced action produced by formic acid can be deleterious to any aluminum exposed to the stripper.

At least about 15%, by volume, dodecylsulfonic acid is necessary to obtain sufficiently rapid photoresist attack, thorough surface cleansing, and miscibility of the chlorinated organic solvents with water. In one sense, I also consider the dodecylsulfonic acids as softening the photoresist for easier removal by the chlorinated solvents. Best results have been obtained with more than about 30% by volume dodecylsulfonic acid. More than about 50% dodecylsulfonic acid appears undesirable in that it may attack aluminum metallization on a silicon slice face.

Substantially equal volumes of the tetrachloroethylene and ortho-dichlorobenzene should be used to obtain the benefits of this invention. In this proportion they are not only effective but stable. They appear to provide benefits not available from either one alone. In general, these should be used in stripper percentages less than about 10 stripper percentage points apart. For example, if the tetrachloroethylene proportion is about 25%, by volume, I would not want the ortho-dichlorobenzene proportion to exceed about 35%, by volume, and vice versa. The combined volumes of the tetrachloroethylene and the ortho-dichlorobenzene should jointly comprise about 50-85% by volume of the stripper, preferably about 50-70%. In equal volumes they would each comprise about 25-42% by volume of the stripper composition, preferably about 25-35% of the mixture.

In general, an equal volume mixture of the two chlorinated organic solvents and the dodecylsulfonic acid can be used, in which each of the three components comprises about one-third of the stripper by volume. Such a stripper would consist of about 30-35% by volume of each of dodecylsulfonic acid, tetrachloroethyl-

ene, and ortho-dichlorobenzene. I prefer the latter two components be present in substantially equal volumes.

In some instances, enhanced stripping speed may be desired. Small amounts of formic acid added to my stripper can be effective in enhancing stripping action. In some instances, about 1% formic acid is needed to sufficiently accelerate stripping action, while in other instances up to 3% may be desired. As hereinbefore indicated, the enhanced stripping action may be aggressive enough to deleteriously affect an aluminum metallization pattern exposed under the photoresist. Accordingly, I would not ordinarily include formic acid in the stripper if any aluminum is exposed to it under the photoresist, as for example an aluminum metallization pattern. Instead, I may choose to include it in the stripper used in earlier process steps, before the aluminum metallization layer is applied. A stripper with formic acid would thus preferably contain by volume about 1-3% formic acid, about 50-84% tetrachloroethylene and ortho-dichlorobenzene and at least 15% dodecylsulfonic acid.

The stripper of this invention is easily handled because it is used under ambient, i.e. room, conditions and because it is miscible with water. In addition, the chlorinated solvents involved are known and handling of them is a generally familiar matter. Further, the stripper rapidly attacks photoresists to produce a complete photoresist removal and a meticulously clean surface removal within minutes. There is no recognizable residue or surface contamination. It does not produce the waste disposal problem associated with photoresist strippers having oxygenated organic solvents such as phenols and cresols. An organic solvent strippable polymer and/or colloid photoresist mask such as KMER, if not completely washed away, is sufficiently softened to permit it to be rinsed away by a subsequent methanol spray. The surface need then only be dried. It is sufficiently clean with the next processing step, even when processing silicon wafers to make integrated circuits. By a methanol spray I mean, for example, a jet of methanol from a nozzle on a plastic squeeze bottle.

A methanol spray is not required, however. For instance, one may choose to instead use a series of successive warm or hot water rinses. Still further, it should be mentioned that my stripper can be used at an elevated temperature if desired, observing usual safeguards, of course. In fact it may be desirable to heat the stripper if the photoresist is particularly difficult to remove, such as an over-cured photoresist.

I should also mention that I have not found any chlorinated organic solvents equivalent to either tetrachloroethylene or ortho-dichlorobenzene for use in my

stripper. Analogously, I have not found any substance that can be substituted for dodecylsulfonic acid in my stripper. In particular, sodium salts of dodecylsulfonic acid would be objectionable. Further, I am not aware of any other organic acid that can be substituted for formic acid.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A low cost and readily disposable liquid composition for removing an organic solvent strippable polymer and/or colloid photoresist mask from a face on a silicon wafer substantially at room temperature and pressure, said composition including, by volume, about 15-50% dodecylsulfonic acid, and about 25-42% of each of tetrachloroethylene and ortho-dichlorobenzene in generally equal stripper proportions.

2. A stripper for removing an organic solvent strippable polymer and/or colloid photoresist mask from a semiconductor device surface, said stripper consisting essentially of, by volume, about 50-85% tetrachloroethylene and ortho-dichlorobenzene in generally equal amounts, up to 3% formic acid, and the remainder substantially dodecylsulfonic acid.

3. A low cost, phenol-less stripper for a hardened, organic solvent strippable polymer and/or colloid photoresist on a silicon wafer surface, said stripper consisting essentially of, by volume, at least about 30% dodecylsulfonic acid, up to 3% formic acid, about 25-35% tetrachloroethylene, and about 25-35% ortho-dichlorobenzene, wherein the stripper percentage of tetrachloroethylene and of ortho-dichlorobenzene are less than about 10 stripper percentage points apart.

4. A low cost, phenol-less stripper for a hardened, organic solvent strippable polymer and/or colloid photoresist material on a silicon wafer face having no unprotected aluminum layer thereon, said stripper consisting essentially of, by volume, about 50-84% tetrachloroethylene and ortho-dichlorobenzene in generally equal amounts, about 1-3% formic acid, and at least 15% dodecylsulfonic acid.

5. A low cost and readily disposable liquid composition suitable for removing a hardened, organic solvent strippable polymer and/or colloid photoresist material from a face on a silicon wafer substantially at room temperature and pressure, which wafer face has an exposed aluminum layer thereon, said composition consisting of about 30-35%, by volume, of each of dodecylsulfonic acid, tetrachloroethylene, and ortho-dichlorobenzene, with the latter two being present in substantially equal volumes.

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[54] METHOD FOR IMPROVING
TRANSPARENCY OF THERMALLY
DAMAGED ACRYLIC GLAZING

[75] Inventors: Reyburn Wick; Kenneth A. Green,
both of Southampton, Pa.

[73] Assignee: The United States of America as
represented by the Secretary of the
Army, Washington, D.C.

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[56] References Cited

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Primary Examiner—Theodore Morris

Attorney, Agent, or Firm—Nathan Edelberg; Robert P.
Gibson; Arthur M. Suga

[57] ABSTRACT

Means for instantaneously temporarily restoring visibility to acrylic glazing of military helicopters where the glazing has been rendered opaqued or frosted by exposure to enemy laser radiation and comprising applying a mixture, preferably 50 percent by volume, of tetrachloroethylene and trichloroethylene to said glazing.

3 Claims, No Drawings

METHOD FOR IMPROVING TRANSPARENCY OF THERMALLY DAMAGED ACRYLIC GLAZING

The invention described herein may be manufactured, used and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

This invention relates to acrylic glazing and more particularly concerns means for immediately, if only transiently, restoring transparency thereto, when rendered opaque or frosted by thermal or laser radiation.

Military helicopters employ canopies of acrylic glazing, such for example as Lucite or Plexiglas, both well-known polymethylmethacrylates, a product of du Pont and Rohm and Haas respectively. Enemy laser radiation can render acrylic glazing unfit for viewing therethrough almost instantaneously. Although past laser efforts for these purposes have been directed principally to 3.8 and 10.6 μm wavelength radiation, any infrared wavelength can frost or opacify acrylic glazing if exposed thereto for a sufficient duration of sufficient wattage. For example, a frosted acrylic surface which will prevent viewing therethrough will occur in less than 1 second if the intensity of the radiation approximates 35-40 watts/cm². Doubling the intensity will approximately halve the time needed before frosting or opacity results to the canopy acrylic glazing. It is apparent therefore that extremely short bursts of high intensity radiation can instantaneously render acrylic glazing unfit for any viewing purposes from military aircraft.

It is therefore an object of this invention to provide means for rendering military canopy acrylic glazing suitable for immediate viewing therethrough, albeit transitory, when said glazing has been thermally damaged by laser radiation.

Other and further objects of the invention will become apparent as the invention is further hereinafter described.

Briefly, we have discovered that polymethylmethacrylate glazing material which has been frosted or opaqued by laser radiation can immediately be made transparent by application thereto of a liquid having a refractive index similar to the acrylic glazing material's refractive index.

More specifically, when a 50 percent by volume mixture of tetrachloroethylene and trichloroethylene are applied to the frosted or opaqued acrylic glazing surface, an immediate and very substantial improvement in the transparency of the acrylic glazing results.

The mixture above-referred to may be applied by any suitable means, its actual method of application forming no part of this invention. Any dispensing means, such for example, as used in automobiles wherein a windshield washing fluid is caused to be applied to dirty windshields has been found to work admirably well with our mixture. The acrylic glazing remains viewable for as long as 15 to 30 seconds after application thereto depending upon speed of the aircraft, ambient temperature, humidity, quantity of mixture applied, and the like. The mixture suffuses the thermally damaged area

instantly to render it once again transparent. The theory or underlying scientific principle which makes our invention operable is believed to reside in the ability of the mixed chloroethylenes to completely and almost instantly fill the voids caused by the laser radiation or to substantially coat the entire damaged surfaces such that little distortion of the light is effected when transmitted therethrough. After the mixture has evaporated to such an extent that visibility is again impaired by the existing laser damage, another application of the mixture to the acrylic glazing will immediately restore its transparency, the procedure being repeated until conditions no longer require the mixture.

The preferred proportions of the volume mixture of tetrachloroethylene and trichloroethylene is about 50 to 50, but any combination thereof which approximates the actual refractive index of the particular acrylic glazing material will be satisfactory. The refractive index of any mixture, of course, may be easily determined by means of a refractometer.

It should be borne in mind that fluids having a lower index of refraction than the acrylic, such as water, ethylene glycol, glycerine, etc., are completely unsatisfactory in temporarily restoring transparency to the damaged acrylic, as well as fluids having higher indices, such as carbon disulfide, ethylenediamine hydrochloride, phenyl p-tolyl ketone, and the like.

It is apparent from the foregoing description that we have provided means readily available to operators of military helicopters whose visibility through acrylic glazing has been substantially impaired by thermal or laser radiation by restoring visibility through the glazing even for a limited time but sufficient for the operator to identify landmarks to thus prevent loss of orientation to the aircraft. And since warfare employing laser radiation is expected to increase markedly, this contribution is considered an important invention in the defense armamentarium of the United States Government.

We claim:

1. Method for rapidly restoring temporary visibility thru acrylic glazing of military helicopters and the like, said glazing having been rendered opaque or frosted by laser radiation, said method comprising

suitably applying a mixture of liquid tetrachloroethylene and liquid trichloroethylene to said glazing such that the refractive index of said mixture approximates the refractive index of said acrylic glazing.

2. The method as described in claim 1 further characterized by the steps of continually repeating said application step whenever said mixture evaporates sufficiently from said acrylic glazing to again present its frosted or opaqued condition.

3. The method as described in claim 1 wherein said mixture comprises about 50 percent by volume of liquid tetrachloroethylene and liquid trichloroethylene.

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